

METHOD 29 – DETERMINATION OF METALS EMISSIONS FROM STATIONARY SOURCES

Check Applicable Analyte	Analyte	Check Applicable Analytical Method Principle			
		ICAP	AAS	GFAAS	ICAP-MS
	Antimony (Sb)				
	Arsenic (As)				
	Barium (Ba)				
	Beryllium (Be)				
	Cadmium (Cd)				
	Chromium (Cr)				
	Cobalt (Co)				
	Copper (Cu)				
	Lead (Pb)				
	Manganese (Mn)				
	Mercury (Hg)				
	Nickel (Ni)				
	Phosphorus (P)				
	Selenium (Se)				
	Silver (Ag)				
	Thallium (Tl)				
	Zinc (Zn)				

Note: The following is only a summary of Method 29 that highlights important aspects of the test methodology. Unless otherwise noted, procedures (i.e. sample train construction, sample recovery, sample preparation, reagents and standards, analytical technique, standards, QA/QC samples, calculations) will strictly be conducted as specified within the most current EPA Method 29 version.

Applicability

This method is applicable to the determination of metals emissions from stationary sources (See previous list). We are aware that the NJDEP does not allow particulate sampling to be combined with the Method 29 train.

Principle

A stack sample is withdrawn isokinetically from the source, particulate emissions are collected in the probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analyzed only for Hg). The recovered samples are digested, and appropriate fractions are analyzed using an analytical method with a sufficient detection limit to demonstrate compliance, as detailed on the previous page.

Interferences

Iron (Fe) can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Aluminum (Al) can be a spectral interference during the analysis of As and Pb by ICAP. Generally, diluting the analytical sample can reduce these interferences, but such dilution raises the in-stack detection limits. Background and overlap corrections may be used to adjust for spectral interferences. Refer to Method 6010 of Reference 2 in Section 16.0 or the other analytical methods used for details on potential interferences to this method. For all GFAAS analyses, use matrix modifiers to limit interferences, and matrix match all standards.

Based on the above we (appropriate box checked):

☐ Do not expect any interference.

☐ Do expect interference. The description and discussion of the anticipated interference follows.

In-Stack Detection Limits & Sample Times

Actual in-stack method detection limits (ISDL) are based on actual source sampling parameters and analytical results. Actual detection limits can be improved through increased stack gas sampled (sample time), reducing the total volume of the digested samples, improving the analytical detection limits or any combination of the three.

The goal of the sample program will be to have the in-stack detection limit at 1/10 the permit allowable expressed as the in-stack concentration limit (ISCL). The ratio of ISCL/ISDL should be ≥ 10 . The following will detail these determinations and will establish the sampling time.

ISDL Calculations for each Analyte

$$\text{ISDL (ug/m}^3\text{)} = A/C \times (B_F + B_B) / 1000$$

Where: A = analytical detection limit (ng/ml)
 B_F = amount of analyte analyzed, front half (ml, default = 300)
 B_B = amount of analyte analyzed, back half (ml, default = 150)
 C = volume of stack gas sampled (m³, 1.25 m³ for each hour)

In-Stack Concentration Limit (ISCL)

$$\text{ISCL (ug/m}^3\text{)} = E/F \times 2.67E8$$

Where: E = permit allowable (lb/hr)
 F = stack flow rate (dscfm)

B_F = _____ B_B = _____ C = _____ F = _____

ANALYTE	A	E	ISDL	ISCL	ISCL/ISDL
Antimony (Sb)					
Arsenic (As)					
Barium (Ba)					
Beryllium (Be)					
Cadmium (Cd)					
Chromium (Cr)					
Cobalt (Co)					
Copper (Cu)					
Lead (Pb)					
Manganese (Mn)					
Mercury (Hg)*					
Nickel (Ni)					
Phosphorus (P)					
Selenium (Se)					
Silver (Ag)					
Thallium (Tl)					
Zinc (Zn)					

*Front-half ISDL calculated by (A x B_F)/C. Back-half ISDL estimated at 0.5 ug/m³. See Sections 13.2 and 11.1.3 of Method 29.

Based on the preceding, each sample run will be _____ minutes.

Sample Train & Recovery Components & Supplies

A schematic of the sampling train is shown in Figure 29-1 of the method. It has general similarities to that of EPA Method 5. Specifically, the sampling train will be constructed with components specified under EPA Method 29, Section 6.0, with the following exceptions and highlights.

No metal components will be used, eliminating potential for metal contamination

Sample Train

- 1) **Probe liner** and **nozzle** will be constructed of glass (Borosilicate or Quartz) or Teflon. A single glass piece consisting of a combined probe tip and probe liner may be used.
- 1) Sample **filters** will be constructed of quartz or glass fiber containing less than $1.3 \mu\text{g}/\text{in}^2$ of each of the metals to be measured. Analytical results provided by filter manufacturers stating metals content of the filters are acceptable.
- 3) The **glass filter holder**, same as Method 5, Section 6.1.1.5, except a **Teflon filter support or other non-metallic support** will be used.
- 4) The **impinger train** (for condensing and collecting gaseous metals and determining the moisture content of the stack gas) will consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is used as a moisture trap. The second impinger (which is the first $\text{HNO}_3/\text{H}_2\text{O}_2$, 5 Percent HNO_3 /10 Percent H_2O_2 , impinger) will be identical to the first impinger in Method 5. The third impinger (which is the second $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger) will be a Greenburg Smith impinger with the standard tip as described for the second impinger in Method 5, Section 6.1.1.8. The fourth (empty) impinger and the fifth and sixth (both containing acidified KMnO_4 , 4 Percent KMnO_4 (W/V), 10 Percent H_2SO_4 (V/V)) impingers are the same as the first impinger in Method 5. A temperature sensor capable of measuring to within 1°C (2°F) will be placed at the outlet of the last impinger. If no Hg analysis is planned, then the fourth, fifth, and sixth impingers are not used. For this test program, the fourth, fifth and sixth impingers (choose one) *will / will not* be used.
- 5) **Teflon Tape** will be used for capping openings and sealing connections, if necessary, on the sampling train.

Sample Recovery

- 1) During sample recovery **non-metallic brushes or swabs** for quantitative recovery of materials collected in the front-half of the sampling train.
- 2) **Glass bottles with Teflon-lined caps** that are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml, for storage of acidified KMnO_4 -containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.
- 3) **Polypropylene Tweezers and/or Plastic Gloves**. Used for recovery of the filter from the sampling train filter holder.

Pre-Test Preparation & Train Assembly

Pre-test preparation will follow the same general procedures given in Method 5, Section 4. All sampling train glassware will be rinsed with hot tap water and then wash in hot soapy water. Next, glassware will be rinsed three times with tap water, followed by three additional rinses with water. Finally, all glassware will be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings will be covered where contamination can occur until the sampling train is assembled for sampling.

The sampling train will be set up as shown in Figure 29-1 of the method. The same general procedures given in Method 5 will be followed, except 100 ml of the $\text{HNO}_3/\text{H}_2\text{O}_2$ solution will be placed in each of the second and third impingers. 100 ml of the acidic KMnO_4 absorbing solution will be placed in each of the fifth and sixth impingers, and approximately 200 to 300 g of pre-weighed silica gel will be transferred from its container to the last impinger.

If Hg analysis will not be performed, the fourth, fifth, and sixth impingers will not be used, if so indicated in the previous section.

SAMPLING

Pre-test leak checks will be conducted followed by three (3) separate and valid isokinetic test runs performed as specified by the procedures given in EPA Method 5. A leak check will be considered valid if the leakage rate is found to be no greater than 0.020 cfm (0.00057 m^3/min) or 4 percent of the average sampling rate (whichever is less). If sampling for Hg, procedures analogous to those described in Section 8.1 of Method 101A, 40 CFR Part 61, Appendix B, will be followed in order to maintain the desired color in the last acidified permanganate impinger. For each run, all required data will be recorded on a data sheet similar to the one shown in Method 5.

Post test leak checks will be conducted at the completion of each test run, with the same acceptance criteria as the pre-test leak check. If the final leak checks are acceptable, then the isokinetic percentages will be calculated as described in Method 5, with an acceptance criteria of 90 to 110 percent.

Sample Recovery

At the completion of each test run the entire sample train will be taken to a **sheltered and contamination free cleanup site**. First, the impingers will be weighed for moisture determination and the following sample fractions will be recovered. All containers will be clearly labeled and the height of

all fluid levels will be marked to ensure no leakage occurred during sample transport. We will also refer to Figure 2, entitled Sample Recovery Scheme, as a general outline.

***Note: We understand the use of the exact method specified rinse volumes is necessary for the subsequent blank correction procedures.**

- 1) Filter removed carefully and placed into petri dish labeled Container No. 1.
- 2) No Container No. 2 because particulate not determined in this sample train.
- 3) Probe, nozzle, and front-half glassware rinsed three times with a total of 100 ml of 0.1N HNO_3 – All placed into a single storage Container No. 3.
- 4) Contents of two $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers and the moisture knockout impinger placed in a container and the volume recorded. Clean each of the three impingers (referring to the 1st originally empty impinger and the 2nd and 3rd impingers containing $\text{HNO}_3/\text{H}_2\text{O}_2$, when a total of 7 impingers are used), the back half of the filter housing, and connecting glassware rinsed three times with a total volume of 100 ml of 0.1 N HNO_3 and label Container No. 4.

When sampling for Hg, steps 5, 6 and 7 are performed.

- 5) Pour all liquid from the impinger preceding the permanganate impingers (impinger No. 4 when a total of 7 impingers are used) into Container No. 5A. Three rinses using a total of exactly 100 ml of 0.1 N HNO_3 are then placed into the same container.
- 6) Place the liquid from the permanganate impingers (impinger Nos. 5 and 6 when a total of 7 impingers used) into Container No. 5B. Three rinses of the impingers and connecting glassware using a total of exactly 100 ml of KNO_3 are then placed in the same container. Place three additional rinses of the impingers and connecting glassware, totaling 100 ml, of water into the same container.
- 7) The permanganate impingers are then rinsed using a total of 25 ml of 8 N HCl . This wash will be placed into a container containing 200 ml of water and labeled Container No. 5C. We understand that this fraction is **required** unless specifically waived by an observer from the Department.
- 8) Silica gel will be placed into Container No. 6. The color of the indicating silica gel will be noted and recorded on the data sheet to determine whether it has been completely spent.

Blank samples for QA/QC purposes, as specified in the method, will be collected in the field and labeled appropriately.

Sample Preparation & Analysis

Sample preparation and analysis will be conducted strictly as specified in Method 29 and the selected analytical method(s). Special attention will be paid to all required QA/QC procedures. On at least one sample run in the source test, and for each metal analyzed, repetitive analysis, Method of Standard Additions, serial dilutions or matrix spike addition will be performed to document the quality of the data.

All analytical fractions will be analyzed **separately**, per the method. We are aware that the NJDEP does not allow the combination of Analytical Fractions 1A and 2A.

Calculations

All calculations will be performed as per Method 29, including blank corrections. Detailed sample calculations will be included in the final report.

Emissions will be presented in the following units: _____.

Proposed Deviations From This BTS Template Or The Method

(Insert any proposed deviations here)